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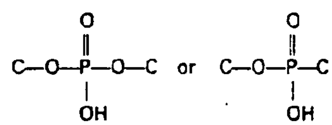
Description

This invention relates to adhesive compositions that adhere strongly to any of the hard tissues of the living body, such as teeth and bones, metallic materials, organic polymers and ceramics, and whose adhesive strength has good water resistance. The term "adhesive compositions" as herein used not only means compositions used for bonding two or more adherends to one another, but also means compositions used for forming highly adhesive coatings on the surfaces of adherends such as metallic materials and organic polymers, and compositions used for forming highly adhesive fillings in the repair of hard tissues of the living body. In other words, the adhesive compositions to which this invention relates comprehend all compositions that exhibit adhesion to and thus are applicable to various kinds of substances, such as the hard tissues of the living body, metallic materials, organic polymers and ceramics.

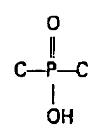
Various kinds of metallic materials, organic polymers and ceramics are used for the restoration of teeth. When these restorative materials are mounted in the mouth, it is necessary to ensure the adhesion between the teeth and the metal, organic polymer or ceramic and also the adhesion of the restorative materials to each other, for example, metal to metal, ceramics or organic polymer. In particular, since dentistry involves use in the mouth, the adhesion must be satisfactory under wet conditions.

Numerous and varied attempts to use phosphate compounds in adhesive compositions have already been made in the dentistry field.

(1) U.S. Patents Nos. 4,259,075, 4,259,117 and 4,368,043 indicate that a polymerizable composition containing a vinyl compound having a group of the formula:



is effective as a dental adhesive. U.S. Patent No. 4,222,780 indicates that a polymerizable composition containing a vinyl compound having a group of the formula:



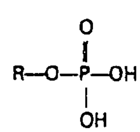
is an effective dental adhesive. Some of the compositions falling within the above patents have been widely used as primers for coating the cavity wall before a tooth cavity is filled. However, there were the problems that the cavity wall must be acid-etched beforehand in order to provide satisfactory adhesive strength to the tooth and that the adhesive strength to a Ni—Cr alloy commonly used in dentistry was not satisfactory.

(2) Attempts to obtain adhesives having adhesion to teeth using polymerizable phosphate compounds have been made, e.g.

(i) U.S. Patent No. 3,882,600 describes phosphoryl monofluoride;

(ii) Journal of Dental Research, vol. 53, p. 878—888 and vol. 56, p. 943—952, Chemical Abstract, vol. 77, p. 290 (66175 g) and Japanese Patent Application Laid-open No. 44152/1976 describe $CH_2{=}CH{-}PO(OH)_2$ and $CH_2{=}CHC_6H_4CH_2PO(OH)_2$;

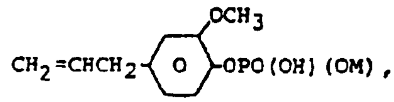
(iii) Japanese Laid-open Patent Application No. 113843/1978 shows compounds obtained by neutralizing one of the two hydroxyl groups in compounds of the formula:

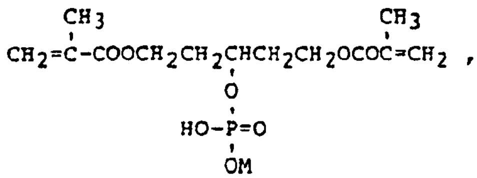


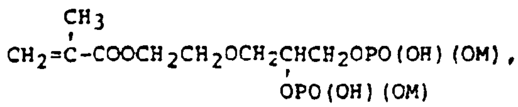
where R represents an organic residue having at least one vinyl group, specific examples of which include the following (where M represents an alkali metal):

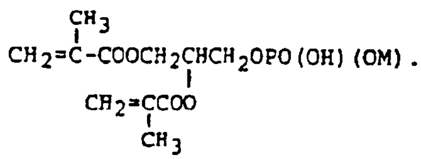
$$CH_2{=}CHC_6H_4OPO(OH)(OM), \quad CH_2{=}\overset{CH_3}{\overset{|}{C}}\text{-}COOCH_2CH_2OPO(OH)(OM),$$

$$CH_2{=}CHCH_2OPO(OH)(OM),$$

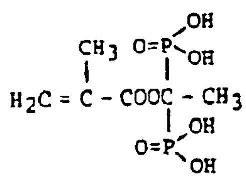








(iv) Japanese Patent Publication No. 49557/1982 describes methacryloyloxyethane-1,1-diphosphonic acid of the following formula:



as an adhesive component in a dental adhesive.

In the case of all the compounds described in (i) to (iv) above, high adhesive strength (especially to metals) under wet conditions cannot be obtained.

European Patent Specification No. EP—A—58483 describes that a polymerizable monomer having a P—Cl bond or P—Br bond is effective as an adhesive component. However, the compounds illustrated in this patent specification do not provide sufficiently high adhesive strength when applied to teeth and metallic materials.

Further, attempts to use phosphate compounds in adhesive compositions have been made widely in various industries. Examples are disclosed in U.S. Patents Nos. 3,754,972, 3,884,864, 3,987,127, 4,001,150, 4,044,044, 4,223,115, Japanese Laid-open Patent Application Nos. 20238/1974, 100596/1975, 125182/1976, 12995/1978, 11920/1981 and 44638/1982, and Japanese Patent Publication Nos. 4126/1980, 4790/1980. However, none of the phosphate compounds described in the above patent literature is free from problems associated with the retention of adhesive strength in the presence of water.

The present invention provides an adhesive comprising

(a) 1 part by weight of a polymerizable monomer represented by the formula:

$$H_2C{=}\overset{R_1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-X_1-R_a-(X_2)_k-\overset{O}{\overset{\|}{\underset{\underset{Z}{|}}{P}}}-Z \qquad (1)$$

in which k is 0 or 1, R_1 is a hydrogen atom or methyl radical; R_a is a C_{6-40} organic residue not containing an

$$H_2C{=}\overset{R_1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-X_1-$$

group and not containing a

$$\begin{array}{c} O \\ \| \\ -P-Z \\ | \\ Z \end{array}$$

group; each of X_1 and X_2, which are the same or different, is an oxa or thia group or a group NR′, where R′ is a hydrogen atom or a C_{1-6} hydrocarbon group, and Z is a halogen atom (F, Cl, Br or I); and

(b) 0 to 199 parts by weight of monomer that is copolymerizable with said monomer (a).

In the adhesive of this invention, the above-mentioned compound of formula (I) is used as a monomer that, on polymerization, imparts adhesive properties. (This monomer may be referred to as adhesive monomer.)

Compositions of the present invention can be used for bonding a hard tissue of the living body with another such tissue or a material for restoring the tissue (for example, a metal, an organic polymer or a ceramic material), or for filling and restoring such a hard tissue (e.g. a tooth), for coating the inside of a cavity of a tooth before filling, for bonding and fixing a tooth and a dental restorative material (e.g. inlay, onlay, abutment, tooth, bridge, post, splint, orthodontic bracket or crown), for bonding dental restorative materials to each other (e.g. abutment tooth and crown), as a pit and fissure sealant for coating a tooth surface to prevent caries, for bonding metals, organic polymers and ceramics, or as adhesives in coating agents or paints to form a coating having excellent adhesion on the surface of a metal or a ceramic material.

As compared with the adhesive monomer exemplified in the abovementioned Japanese Laid-open Patent Specification No. 161607/1982, the adhesive monomer of the adhesive of this invention has an R_a of higher carbon number. The Japanese Patent Specification does not mention that the adhesive strength is greatly affected by the carbon number of the organic residue connecting the polymerizable group having a double bond and the $-POCl_2$ or $-POBr_2$ group, whereas the present inventors unexpectedly found that as the carbon number of R_a is increased, the resulting adhesive firmly adheres not only to teeth, but also to metallic and ceramic materials.

The term "organic residue' is used herein to denote an organic residue made up of a carbon skeleton which may have a hetero atom (O, S, N or P), preferably

(i) a C_{6-30} hydrocarbon group, optionally having a hydroxy, carboxy or halogen (F, Cl, Br or I) substituent; or

(ii) a C_{9-30} organic residue in which from two to seven C_{1-29} hydrocarbon groups, at least one of which has 3 or more carbon atoms, optionally having a hydroxy, carboxy or halogen substituent, are connected to one another through a

$$-O-,\ -S-,\ -\overset{\overset{\displaystyle O}{\|}}{C}-O-,\ -\overset{\overset{\displaystyle S}{\|}}{C}-O-,\ -\overset{\overset{\displaystyle O}{\|}}{C}-S-,\ -\overset{\overset{\displaystyle O}{\|}}{C}-,\ -\overset{\overset{\displaystyle S}{\|}}{C}-,\ -\overset{\overset{\displaystyle R'}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-,$$

$$-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-,\ -\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-,\ -N<,\ \text{or}\ -O-\overset{\overset{\displaystyle O}{\|}}{P}\!<\!\begin{array}{l} O- \\ O- \end{array}$$

linkage (where R′ is as defined above).

Organic residues having the above structure (ii) include those in which the main chain is made up of two or more hydrocarbon groups and some of the hydrocarbon groups constitute the side chain of the skeleton. Illustrated below are the hydrocarbon groups (represented by A) connected through the linkage (represented by B). For simplicity, groups having the double bond are shown as [C=C] and oxyhalogenated phosphorus is shown as [P].

$$[C{=}C]-A_1-[P]$$

$$[C{=}C]-A_1-B_1-\underset{\underset{\displaystyle [P]}{|}}{A_2}-B_2-A_3-[C{=}C]$$

$$[C{=}C]-A_1-\underset{\underset{\displaystyle A_3}{|}}{B_1}-A_2-[P]$$

$$\begin{array}{l} [C{=}C]-A_1-B_1-A_2-B_2-A_3-[P] \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad B_3 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad A_4 \end{array}$$

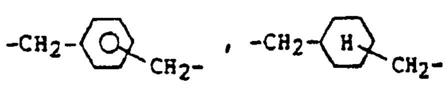
$$\begin{array}{l} [C{=}C] \\ \qquad\quad >A_1-B_1-A_2-[P] \\ [C{=}C] \qquad\ \ |\qquad | \\ \qquad\qquad\ \ A_3\quad B_2 \\ \qquad\qquad\qquad\ \ | \\ \qquad\qquad\qquad\ \ A_4 \end{array}$$

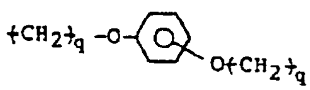
$$\begin{array}{l} \qquad\qquad\qquad\quad A_4 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad B_3 \\ \qquad\qquad\qquad\quad | \\ [C{=}C]-A_1-B_1-A_2-B_2-A_3-[P] \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad B_4 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad A_5 \end{array}$$

The term "hydrocarbon group" as used in this specification includes halogenated hydrocarbon groups, unless otherwise noted.

The above-mentioned compound (I) exhibits the highest adhesive strength and firmly adheres to teeth, metallic materials, and ceramic materials when k is 1, X_1 and X_2 are —O—, and R_a is:

(i) $-(CH_2)_n-$ [where n is an integer from 6 to 20.]

(ii)  , or $-CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2-$

(iii)  [where q is 2, 3, or 4.]

$$\begin{array}{l} -CH_2CH- \\ \quad\ \ | \\ \quad CH_2O(CO)_p-R_b \end{array} \qquad \text{(iv)}$$

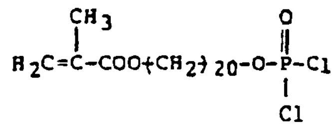
[where p is 0 or 1, and R_b is a C_{3-16} hydrocarbon group.]

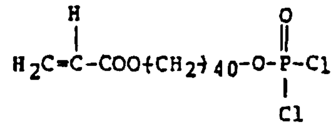
Examples of the adhesive monomer used in this invention are shown below.

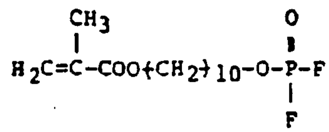
$$\begin{array}{l} \quad\ CH_3 \qquad\qquad\qquad\quad O \\ \quad\ | \qquad\qquad\qquad\qquad\ \ \| \\ H_2C{=}C-COO-(CH_2)_6-O-P-Cl \\ \qquad\qquad\qquad\qquad\qquad\ \ | \\ \qquad\qquad\qquad\qquad\qquad\ Cl \end{array}$$

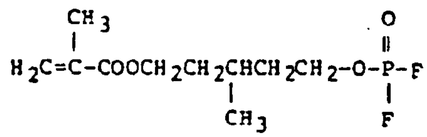
$$\begin{array}{l} \quad\ CH_3 \qquad\qquad\qquad\quad O \\ \quad\ | \qquad\qquad\qquad\qquad\ \ \| \\ H_2C{=}C-COO-(CH_2)_8-O-P-Br \\ \qquad\qquad\qquad\qquad\qquad\ \ | \\ \qquad\qquad\qquad\qquad\qquad\ Br \end{array}$$

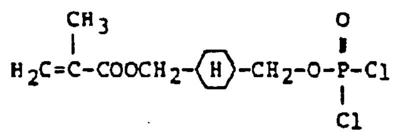
$$\begin{array}{l} \quad\ CH_3 \qquad\qquad\qquad\quad\ \ O \\ \quad\ | \qquad\qquad\qquad\qquad\quad \| \\ H_2C{=}C-COO-(CH_2)_{10}-O-P-Cl \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\ \ Cl \end{array}$$

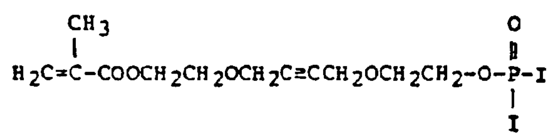


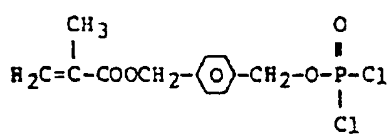


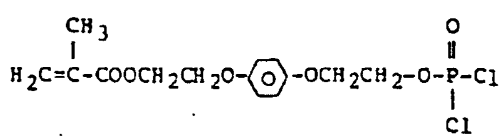


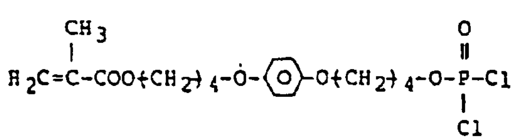


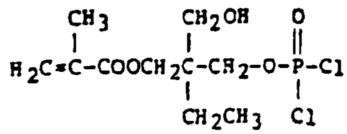


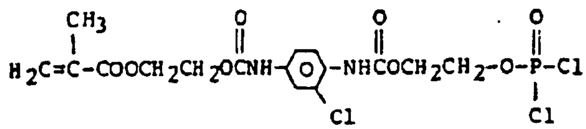


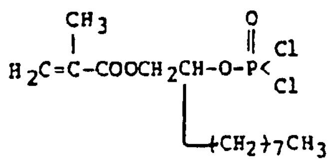


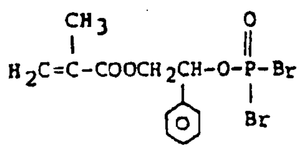


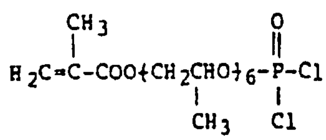


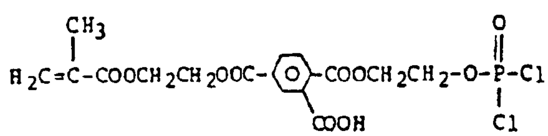


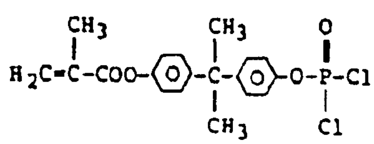


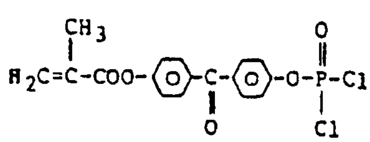


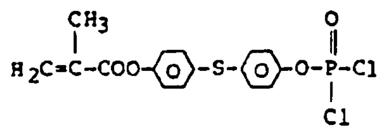


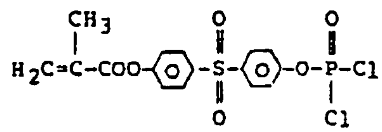


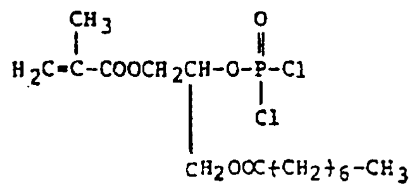


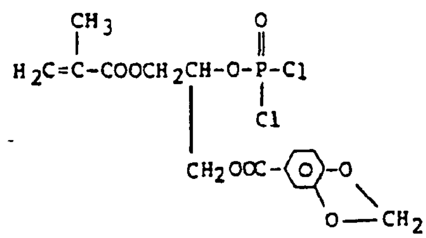


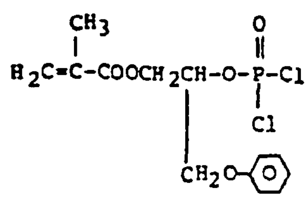


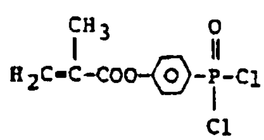


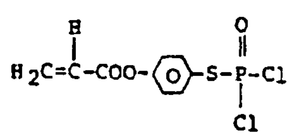


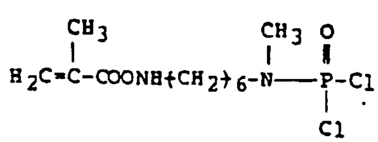


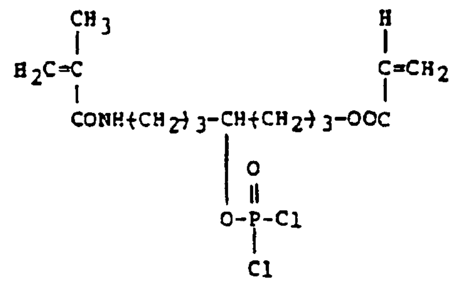


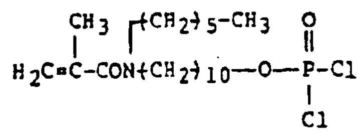


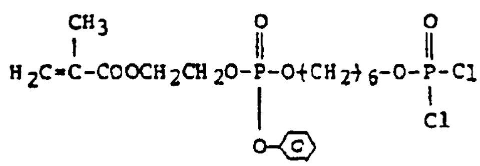


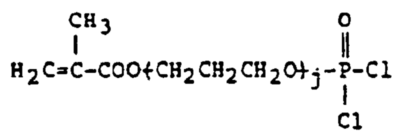




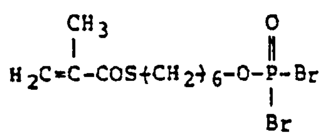


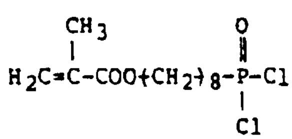


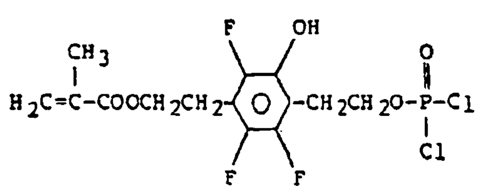


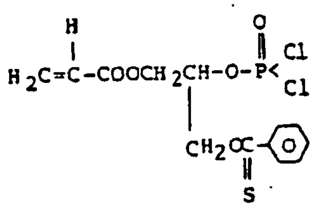


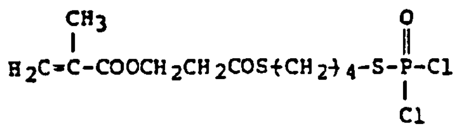
(where j = 2 to 10)

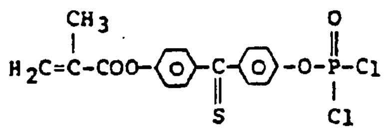


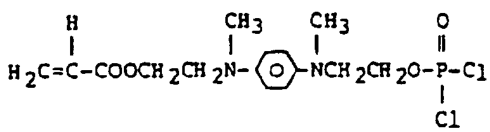


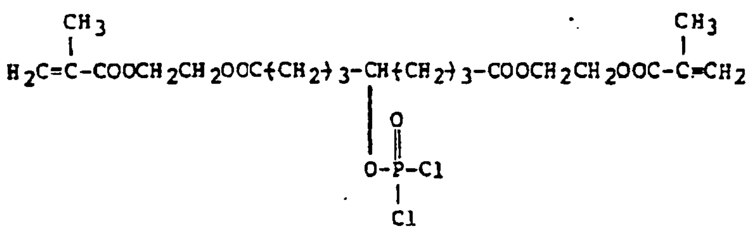


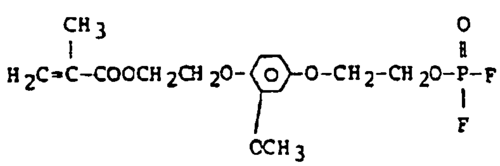


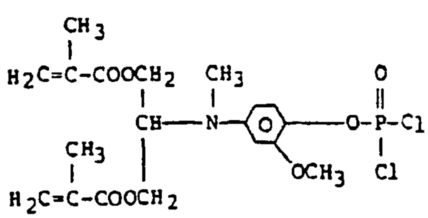


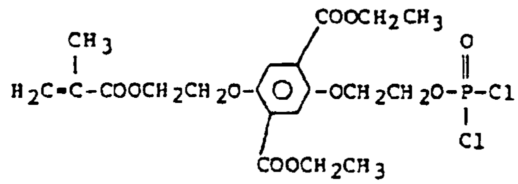


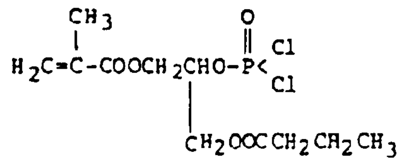


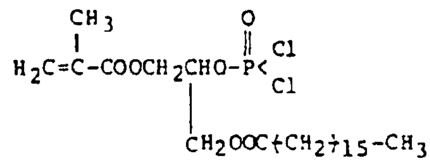






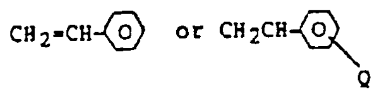






In the case where R_a in the compound of formula (I) has a carbon number of 4 or less, the resulting adhesive is extremely poor in adhesion to teeth, metallic materials, and ceramic materials and is also poor in water resistance of adhesive strength, as compared with the adhesive of this invention. In general, there is a tendency that as the carbon number of R_a increases, the resulting adhesive increases in adhesive strength. When R_a has the carbon number 6, the desired result is achieved; and when R_a has the carbon number 8 to 20, the adhesive exhibits the highest adhesive strength. As the carbon number of R_a increases more than 40, the resulting adhesive becomes poor in adhesive strength. Therefore, it is necessary that the carbon number of R_a should be less than 40.

The adhesive of this invention is formed by mixing the compound of formula (I) with a vinyl monomer copolymerizable with the compound. The copolymerizable monomer affects the viscosity, wettability, curability, and mechanical properties of the adhesive. Thus it should be properly selected according to the intended use of the adhesive. Usually, it is (meth)acrylate type monomer, styrene type monomer, or vinyl acetate. The monomer is not limited to them, however. It also includes (meth)acrylamide, N-n-butoxymethyl(meth)acrylamide, N-(hydroxymethyl)acrylamide, and other acrylamides; and (meth)acrylic acid, isobutylvinyl ether, diethyl fumarate, diethyl maleate, maleic anhydride, methyl vinyl ketone, allyl chloride, vinyl naphthalene, and vinylpyridine. The above-mentioned styrene type monomer includes those compounds (such as divinyl benzene and p-chlorostyrene) represented by



(where Q denotes a halogen or a C_{1-8} hydrocarbon group). The (meth)acrylate type monomer is one which is commonly used for anaerobic adhesives and dental adhesives. It is a (meth)acrylate monomer represented by

$$\left(CH_2{=}\overset{\overset{\displaystyle R_1}{|}}{C}H{-}COO\right)_t{-}U$$

(wherein R_1 denotes H or CH_3, U denotes a C_{1-50} organic group, t denotes an integer of 1 to 4, and the organic group is defined above). Examples of such monomer include the following.

(i) Monofunctional (meth)acrylate

Methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, decyl (meth)acrylate, lauryl

(meth)acrylate, stearyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate (HEMA), 2-hydroxypropyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 3-chloro-2-hydroxypropyl methacrylate, and 2,3-dibromopropyl (meth)acrylate.

(ii) Difunctional (meth)acrylate

a) One in which U is $—CH_2CH_2(OCH_2CH_2)_s—$ or

$$—CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H(OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_s—$$

(where s is an integer of 0 to 15)

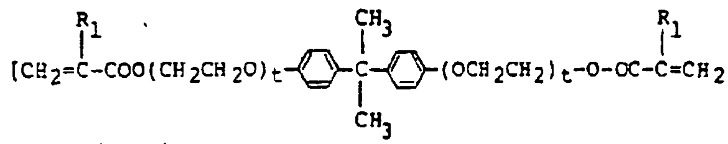
Ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)-acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, and tripropylene glycol di(meth)acrylate.

b) One in which U is an alkylene of carbon number 3 to 12

Propanediol di(meth)acrylate, glycerin di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,5-pentanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl-glycol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, and 2,3-dibromoneopentyl glycol dimethacrylate.

c) One in which U has a residue of bisphenol-A derivative

Bisphenol-A di-(meth)acrylate, 2,2-bis[(meth)acryloyloxy polyethoxyphenyl]propane,



where t is an integer of 1 to 9],

2,2'-bis(4-acryloyloxy propoxyphenyl)propane, and 2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)-phenyl]propane (Bis-GMA). Preferable among them are those in which U has a carbon number 15 to 30.

d) One in which U is

$$—CH_2\overset{\displaystyle OH}{\overset{|}{C}}HCH_2O(CH_2CH_2)_uOCH_2\overset{\displaystyle OH}{\overset{|}{C}}HCH_2—$$

(wherein u is 1 or 2)

1,2-bis[3-(meth)acryloyloxy-2-hydroxypropoxy]ethane, and 1,4-bis[3-(meth)acryloyloxy-2-hydroxypropoxy]butane.

e) One in which U is JOCONHTNHCOOJ [where J denotes a C_{2-10} alkylene, and T denotes an organic diisocyanate residue of carbon number 1 to 60].

Urethane di(meth)acrylate, as disclosed in Japanese Patent Laid-open No. 687/1975.

(iii) Tri- and tetrafunctional methacrylates

Trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, and N,N'-(2,2,4-trimethylhexamethylene) bis [2-aminocarboxy)propane-1,3-diol]tetra-methacrylate.

The above-mentioned copolymerizable monomers are used individually or in combination with one another. The most preferred one for dental adhesive is methacrylate ester, and it should preferably account for more than 50 wt% of the total copolymerizable monomer. Preferred examples of methacrylate ester include methyl methacrylate, ethyl methacrylate, HEMA, n-hexyl methacrylate, benzyl methacrylate, lauryl methacrylate, bis-GMA, bisphenol-A dimethacrylate, 2,2-bis[(meth)acryloyloxy polyethoxyphenyl]-propane, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, 1,10-decanediol dimethacrylate, neopentyl glycol dimethacrylate and trimethylolethane trimethacrylate.

In the adhesive of this invention, the compound of formula (I) should be contained more at than 0.5 wt% in the total polymerizable monomer; in other words, the above-mentioned copolymerizable monomer should be used in an amount of 0 to 199 parts by weight for 1 part by weight of the compound of formula (I). If the content of the compound of formula (I) is less than 0.5 wt%, the resulting adhesive is insufficient in adhesive strength. The compound of formula (I) should preferably be used more than 1.5 wt%.

The adhesive of this invention exhibits its adhesive strength when polymerized and cured after application to the adherend or filling into the cavity. The curing is accomplished physically with heating or irradiation of X-rays, ultraviolet rays, or visible light, or chemically with a polymerization initiator. Usually,

the adhesive is incorporated with a photosensitizer or a polymerization initiator to facilitate curing. They are collectively called a curing agent in this invention. The curing agent that can be used in this invention includes organic peroxides, azo compounds, organometallic compounds, redox initiators, and photosensitizers for ultraviolet rays and visible light. Their examples include benzoyl peroxide, di-t-butyl peroxide, cumene hydroperoxide, t-butylhydroperoxide, methyl ethyl ketone peroxide, azobisisobutyronitrile, organic sulfinic acid (or salt thereof), tributyl borane, hydrogen peroxide/Fe^{2+} salt, cumene hydroperoxide/Fe^{2+} salt, benzoyl peroxide/N,N-dialkylaniline derivative, ascorbic acid/Cu^{2+} salt, organic sulfinic acid (or salt thereof)/amine (or salt thereof)/peroxide, α-diketone/allylthiourea (visible light curing), benzoin methyl ether, benzoinethyl ether, benzyl, diacetyl, diphenyldisulfide, and di-β-naphthyl sulfide. Preferable among them are benzoyl peroxide, azobisisobutyronitrile, tributyl borane, and organic sulfinic acid (or salt thereof)/diacyl peroxide/aromatic secondary or tertiary amine (or salt thereof). The aromatic sulfinic acid includes benzenesulfinic acid, p-toluenesulfinic acid, β-naphthalenesulfinic acid, and styrenesulfinic acid. The cation which forms a salt with the sulfinic acid is an alkali metal ion, alkaline earth metal ion, or ammonium ion. The former two preferred from the standpoint of storage stability and adhesive strength. Their examples are Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and Sr^{2+}. The preferred examples of aromatic amines include N,N-dimethylaniline, N,N-dimethyl-p-toluidine, N,N-diethanolaniline, N,N-di-ethanol-p-toluidine, N-methylaniline, and N-methyl-p-toluidine. These amines may form a salt with hydrochloric acid, acetic acid, or phosphoric acid. The diacyl peroxide includes benzoyl peroxide, m-toluoylperoxide, 2,4-dichlorobenzoyl peroxide, octanoyl peroxide, lauroyl peroxide, and succinic acid peroxide. Preferable among them are benzoyl peroxide and m-toluoyl peroxide. These curing agents are added in an amount of 0.01 to 20 parts by weight, preferably 0.1 to 15 parts by weight, for 100 parts by weight of the polymerizable monomer.

In some cases, it is desirable to incorporate the adhesive of this invention with a volatile organic solvent having a boiling point lower than 150°C at 101 KPa (760 Torr). Such an embodiment is preferable where the adhesive of this invention is used as a primer to be applied to the tooth cavity prior to the filling of a dental filling material. After application, the volatile organic solvent is vaporized by blowing air or nitrogen so that a film of the adhesive is formed on the adherend. The preferred organic solvent includes methanol, ethanol, acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, dichloromethane, chloroform, ethyl ether, isopropyl ether, and toluene. The volatile organic solvent is used in an amount of less than 300 times (by weight), preferably less than 100 times, the weight of the total polymerizable monomer. Dilution in excess of 300 times results in a great decrease in adhesive strength due to an excessively thin film of polymerizable monomer formed after the volatilization of the solvent.

The adhesive of this invention may be incorporated with a known filler (inorganic, organic polymer, or inorganic-organic comosite type). When incorporated with a filler, the adhesive of this invention can be used as a dental cement (for adhesion and filling), dental composite resin, and bone cement. The filler should be added in an amount of less than 1000 parts by weight, preferably 20 to 500 parts by weight, for 100 parts by weight of the polymerizable monomer. The filler improves the rheological properties of the adhesive composition at the time of its use, the mechanical properties of the cured adhesive, and the adhesive strength and the resistance of the adhesive strength to water. Examples of the inorganic filler include natural minerals such as quartz, felstone, pottery stone, wall-astonite, mica, clay, kaolin, and marble; ceramics such as silica, alumina, silicon nitride, boron carbide, boron nitride, soda glass, barium glass, strontium glass, borosilicate glass, and lanthanum-containing glass ceramic; and water-insoluble inorganic salts such as barium sulfate and calcium carbonate. Usually, the inorganic filler undergoes surface treatment with a silane coupling agent such as γ-methacryloyloxypropyl trimethoxy silane, vinyl trimethoxy silane, vinyl triethoxy silane, vinyl trichlorosilane, vinyl tris(2-methoxyethoxy)silane, vinyl triacetoxy silane, and γ-mercaptopropyl trimethoxy silane. The organic polymeric filler includes polymethyl methacrylate, polyamide, polyester, polypeptide, polysulfone, polycarbonate, polystyrene, chloroprene rubber, nitrile rubber, styrene-butadiene rubber, and polyvinyl acetate. The inorganic-organic composite type filler includes the silane-treated inorganic filler coated with the above-mentioned polymer.

These fillers are used individually or in combination with one another. The filler may be of formless, spherical, lamellar, or fibrous, having a particle diameter smaller than 100 μm. The polymeric filler may be dissolved in the polymerizable monomer or a volatile organic solvent. Inorganic fillers and inorganic-organic composite type fillers are preferable where the adhesive of this invention is used as a dental cement or dental composite resin, and organic fillers are preferable where it is used as a bone cement.

In the case where the adhesive of this invention is intended for industrial use and home use, the adhesive may be incorporated with an organic solvent-soluble polymer such as PMMA, polystyrene, polyvinyl acetate, chloroprene rubber, butadiene rubber, nitrile rubber, and chlorosulfonated polyethylene in an amount of less than 200 parts by weight, preferably less than 120 parts by weight, for 100 parts by weight of the vinyl monomer composition, whereby the adhesive is increased in viscosity and the mechanical properties of the cured adhesive are improved.

In addition to the above-mentioned additives, the adhesive of this invention may be incorporated with a polymerization inhibitor [e.g., hydroquinone methyl ether (MEHQ)], antioxidant [e.g., 2,6-di-tert-butyl-p-cresol (BHT)], ultraviolet absorbing agent, pigment, phthalic acid diester, silicone oil, etc, as occasion demands, according to the performance required. These additives are added in an amount of less than 10

parts by weight, preferably less than 5 parts by weight, for 100 parts by weight of the polymerizable monomers.

In the case where the adhesive of this invention is used in the dentistry and orthopedics, a redox initiator of room temperature curing type is commonly used. In such a case, the oxidizing agent and the reducing agent should be packed separately to ensure storage stability, and a special attention should be paid to the package form. Examples of the package form include the two-pack systems, each pack containing vinyl compound plus reducing agent and vinyl compound plus oxidizing agent; vinyl compound plus oxidizing agent (or reducing agent) and volatile organic solvent plus reducing agent (or oxidizing agent); vinyl compound plus oxidizing agent (or reducing agent) and filler plus reducing agent (or oxidizing agent); or vinyl compound plus filler plus oxidizing agent and vinyl compound plus filler plus reducing agent. In the case of the three-component system composed of organic sulfinic acid (or salt thereof)/amine (or salt thereof)/peroxide, which is most suitable for the adhesive of this invention, the sulfinic acid and amine function as the reducing agent and the peroxide, as the oxidizing agent. In this case, a three-pack system may be employed in which the sulfinic acid and amine are separated from each other.

In the case where a photosensitizer is used as a curing agent, the package containing the vinyl compound and photosensitizer should be stored in a container shielded against light. In the case where an initiator (such as tributyl borane) is employed which initiates polymerization in a short time on contact with the vinyl compound, the initiator and the vinyl compound should be packed separately from each other. The two-pack adhesive composition is mixed together immediately before use.

The adhesive of this invention exhibits outstanding adhesion for a variety of materials as enumerated below, and keeps the high adhesive strength under a wet condition over a long period of time.

(i) Hard tissues of the living body, such as teeth and bones.

(ii) Base metals and alloys thereof such as iron, nickel, chromium, cobalt, aluminum, copper, zinc, tin, stainless steel, and brass; and noble metal alloys containing 50 to 90% of gold or platinum, which are difficult to bond with a conventional adhesive.

(iii) Ceramics such as glass, porcelain, silica, and alumina.

(iv) Organic polymers such as polymethyl methacrylate, polyester, polyamide, polyurethane, polycarbonate, polysulfone, and polystyrene.

Because of its ability to exhibit high adhesive strength for a variety of materials as mentioned above, the adhesive of this invention will find use in various application areas. Examples of preferred applications are as follows:

(i) Dentistry

The adhesive is applied to the wall of a tooth cavity to be filled with a composite resin which is usually composed of a polymerizable monomer, filler, and polymerization initiator. When supplied to the dentist, the adhesive is combined with the composite resin to form a system.

The adhesive composition incorporated with a filler is used as a composite resin to be filled in the tooth cavity. Not only does the adhesive composition function as a filling material but also it firmly adheres to the tooth.

The adhesive is used to bond an inlay, onlay, or abutment to a tooth cavity; to fasten a bridge, post, splint, or orthodontic bracket to teeth; or to bond a crown to an abutment.

The adhesive is used as a pit fissure sealant.

For each application, the specific composition of the adhesive is selected as mentioned above. For example, if the adhesive is to be coated on a tooth prior to the filling of a composite resin, the adhesive composition may be prepared according to the recipe as shown in U.S. Patent Specifications US—A—4,259,075 and 4,259,117. That is, the adhesive composition is made up to 1.5 to 100 wt% of the above-mentioned vinyl compound (which exhibits adhesion on polymerization), a polymerizable monomer (such as bis-GMA, HEMA, and aliphatic dimethacrylate), an organic solvent (such as ethanol) as a diluent, and a curing agent of room temperature curing type. Also, if the adhesive composiiton is to be used in the form of a composite resin, it is prepared according to the recipe shown in the above-mentioned U.S. Patents Specifications. That is, the above-mentioned adhesive vinyl compound is added in an amount of 1.5 to 50 wt% (based on the total polymerizable monomers) to a conventional filler material composed of 20 to 40 wt% of polymerizable monomer (such as bis-GMA) and 80 to 60 wt% of filler.

The adhesive thus prepared is applied to a tooth in the usual way. On curing, the composite resin adheres to a tooth so firmly that it is not necessary to provide mechanical retention such as undercut. (It is preferable to subject the tooth surface to acid etching before the adhesive of this invention is applied to the tooth; however, it provides practically sufficient adhesive strength without acid etching, unlike the compositions disclosed in the US—A—4,259,075 and 4,259,117. There is some fear for the injurious effect of acid etching on the dentin.)

The adhesive composition to bond an inlay, onlay, or crown to a tooth cavity or abutment should preferably be composed of 1.5 to 50 parts by weight of the adhesive vinyl monomer, 98.5 to 50 parts by weight of the copolymerizable monomer, and 50 to 500 parts by weight of filler. With the adhesive composition thus prepared, it is possible to achieve the bonding of an inlay, onlay, or crown to a tooth cavity, which could not be achieved with a conventional luting cement.

In an additional application in the dentistry, a liquid composed of the adhesive vinyl monomer,

copolymerizable monomer, and curing agent is applied to the tooth surface, followed by curing, so that the firmly-bonding film formed on the tooth surface prevents tooth decay.

(ii) Orthopedics

The adhesive composition of this invention will find use as a bone cement to bond a ceramic or metallic artificial joint or splint to a bone. The adhesive composition for such use should preferably be composed of 90 to 98.5 parts by weight of methyl methacylate, 10 to 1.5 parts by weight of adhesive vinyl monomer, and 50 to 150 parts by weight of filler (e.g., PMMA).

(iii) General industrial and home uses

Because of its outstanding adhesion to metals, ceramics, and organic polymers, the adhesive of this invention will find general use in the areas of transport, electric machines, building materials, can manufacture, ceramic industry, and home appliances. It will also find use as a coating material such as a paint and an under coating. When used for coating, it adheres much more firmly to the substrate than the existing adhesive of polymerization curing type (such as cyanoacrylate, epoxy resin, and second-generation acrylic adhesive), even if the substrate is stained with oil or wetted. This is a surprising feature of the adhesive of this invention.

Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are intended for purpose of illustration only and are not intended to be limiting.

Production Example 1

The adhesive monomer used in this invention was prepared as follows: Into a 200-cc three-neck flask were charged 56 g of methacrylic acid, 76 g of 1,6-hexane-diol, 6 g of p-toluenesulfonic acid, and 0.2 g of MEHQ. The reactants were heated to 85°C under a reduced pressure of 23 KPa (170 mmHg), and the reaction was carried out for several hours, while blowing oxygen, until water was not distilled any longer. The reaction liquid was cooled to room temperature and then transferred to a separatory funnel. The reaction liquid was washed with 5% aqueous solution of sodium carbonate until the washings became alkaline. The reaction liquid was further washed with five 100 cc portions of neutral water. After dehydration with anhydrous sodium sulfate, the reaction liquid, with 12 mg of MEHQ added, was heated to 80°C under reduced pressure to remove the residual water. Thus there was obtained 74 g of a mixture of 1,6-hexanediol monomethacrylate and 1,6-hexanediol dimethacrylate. The analysis by high-performance liquid chromatography (HLC) showed that the content of monoester was 75 mol% and the residual quantity of feedstock diol was less than 0.5 wt%.

Into a 500 cc reactor was charged 22.9 g of phosphorus oxychloride dissolved in 100 cc of ethyl ether, followed by cooling to −50°C. 40.5 g of the previously prepared methacrylic ester mixture ad 15.4 g of triethylamine, both dissolved in 100 cc of ethyl ether, were added slowly dropwise, through a 200 cc dropping funnel connected to the reactor, to the phosphorus oxychloride solution, with vigorous stirring, while blowing dry nitrogen. After dropping was complete, the reaction liquid was kept at −30°C for 3 hours, and then the reaction liquid was warmed to room temperature. The triethylamine hydrochloride which had separated out was filtered off by a glass filter. To the filtrate was added 40 mg of MEHQ and the ethyl ether was distilled away under reduced pressure to give nonvolatile liquid residue. Dimethacrylate in the residue was extracted out with four 200 cc portions of n-hexane, and then residual n-hexane in the residue was distilled away under reduced pressure. Thus there was obtained 32 g of oily substance. It was confirmed by elemental analyses and H^1— and P^{31}—NMR that the oily substance is a compound of the following formula:

$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}COO{+}CH_2{+}_6{-}O{-}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle Cl}{|}}{P}}}{-}Cl \qquad (A)$$

Production Example 2

The adhesive monomer used in this invention was prepared as follows: Into a 500-cc three-neck flask were charged 56 g of methacrylic acid, 92 g of 1,10-decanediol, 6 g of p-toluenesulfonic acid, and 0.2 g of MEHQ. The reactants were heated to 80°C to make a uniform solution. The flask was evacuated to 150 mmHg, and the esterification reaction was carried out at 90°C while blowing oxygen with stirring. The reaction was ceased when water was not distilled away any longer. After cooling to room temperature, the reaction liquid was diluted with 150 cc of n-hexane. The solids which separated out on dilution were filtered off, and the filtrate was washed with an aqueous solution of sodium carbonate until the washings became alkaline. After repeated washing with water, the reaction liquid was diluted with 500 cc of n-hexane. The reaction liquid was allowed to stand at 5°C, with anhydrous sodium sulfate added thereto. One day later, the unreacted diol which had separated out during standing were filtered off again. The filtrate, with 10 mg of MEHQ added, was heated to 80°C under reduced pressure to remove n-hexane. Thus there was obtained

110 g of a mixture of methacrylate monoester and diester of 1,10-decanediol. The analysis by HLC showed that the content of monoester was 65 mol% and only a trace of unreacted diol was contained.

Into a 500 cc reactor was charged 22.9 g of phosphorus oxychloride dissolved in 100 cc of ethyl ether, followed by cooling to −50°C. 81.5 g of the previously prepared ester mixture and 15.4 g of triethylamine, both dissolved in 120 cc of ethyl ether, were added slowly dropwise, through a 300 cc dropping funnel connected to the reactor, to the phosphorus oxychloride solution, with vigorous stirring, while blowing dry nitrogen. After dropping was complete, the reaction liquid was kept at −30°C for 3 hours, and then the reaction liquid was warmed to room temperature. The triethylamine hydrochloride which had separated out was filtered off by a glass filter. To the filtrate was added 40 g of MEHQ and the ethyl ether was distilled away under reduced pressure to give nonvolatile liquid residue. Dimethacrylate in the residue was extracted out with four 200 cc portions of n-hexane, and then residual n-hexane in the residue was distilled away under reduced pressure. Thus there was obtained 37 g of oily substance. It was confirmed by elemental analyses and H^1— and P^{31}—NMR that the oily substance is a compound of the following formula:

$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}COO{+}CH_2{+}_{10}{-}O{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle O}{\overset{\|}{P}}}}{-}Cl \qquad (B)$$

Example 1

A two pack primer of the following composition was prepared from the compound (B) synthesized in Production Example 2.

	Parts by weight
Formulation 1.	
2,2-Bis[methacryloyloxypolyethoxyphenyl]propane	55
Triethylene glycol dimethacrylate	35
Compound (B)	10
Benzoyl peroxide	2
Formulation 2.	
Ethanol	100
Sodium benzenesulfinate	3
N,N-diethanol-p-toluidine	1

A specimen for adhesion was prepared by embedding a human molar in an epoxy resin in a cylindrical holder and then cutting the crown so that the dentin was exposed. On the other hand, a quadrangular prism of water-containing ivory measuring 10 × 10 × 30 mm was provided. The surface of the dentin and the end of the ivory prism were polished with #1000 sand paper. The polished surface of the dentin was covered with a piece of adhesive tape having a hole 5 mm in diameter. This hole establishes the area of adhesion. Formulation 1 and formulation 2 were mixed in equal quantities, and the mixture was applied to the dentin surface and the end of the ivory prism. Immediately, air was blown to the coated surface by using an air syringe to vaporize ethanol. A commercial dental composite "Clearfil-F" was mixed and the resulting paste was cast up on the end of the ivory prism. The ivory prism was pressed against the surface of the dentin, with the paste interposed between the two surfaces. After being kept pressed for 30 minutes, the dentin specimen and the ivory prism which had been bonded together were dipped in water at 37°C for one day. Tensile bonding strength was measured. The bonding strength was 7 MPa (70 kg/cm²) when failure occurred at the dentin-composite resin interface.

Comparative Example 1

Example 1 was repeated except that the compound (B) was replaced by the compound (C) of the following formula which is described in Japanese Laid-open No. 151607/1982.

$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}COOCH_2CH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{P}}{<}{\begin{matrix}Cl\\Cl\end{matrix}} \qquad (C)$$

The tensile bonding strength was 0.4 MPa (4 kg/cm²).

Example 2

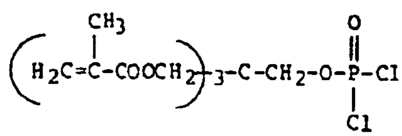
A powder-liquid type adhesive of the following composition was prepared from the compound (A) synthesized in Production Example 1.

	Parts by weight
Formulation 3.	
Methyl methacrylate	97
Compound (A)	3
Benzoyl peroxide	2
MEHQ	trace amount
Formulation 4.	
Polymethyl methacrylate powder	100
Sodium benzenesulfinate	5
N,N-diethanol-p-toluidine	2

According to the method as described in Example 1, a specimen of dentin of a human tooth and an ivory prism were provided. Formulation 3 and formulation 4 were mixed in equal quantities. The resulting viscous slurry was applied to the dentin surface covered with a piece of adhesive tape having a hole 5 mm in diameter and to the end of the ivory prism. The dentin specimen and the ivory prism were pressed against each other. After being kept pressed for 30 minutes, they were dipped in water at 37°C for one day. Tensile bonding strength was measured. The bonding strength was 6 MPa (62 kg/cm²) when failure occured at the dentin-resin interface.

Comparative Example 2

Example 2 was repeated except that the compound (A) was replaced by the compound (D) of the following formula.



(D)

The tensile bonding strength to dentin measured according to the method of Example 2 was 1.3 MPa (13 kg/cm²).

Example 3

A powder-liquid type adhesive of the following composition was prepared from the compound (B) synthesized in Production Example 2.

	Parts by weight
Formulation 5.	
Methyl methacrylate	97
Compound (B)	3
Benzoyl peroxide	2
MEHQ	trace amount
Formulation 6.	
Polymethyl methacrylate powder	100
Sodium benzenesulfinate	5
N,N-diethanol-p-toluidine	2

The resulting adhesive was evaluated with respect to adhesion to the dental Ni—Cr alloy (Ni: 92.7%, Cr: 6%, and others: 1.3%) and the dental porcelain (Vita VMK 68, No. 511P).

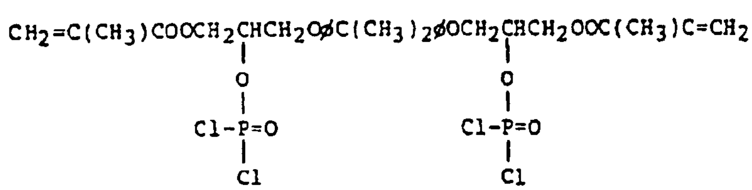
The Ni—Cr alloy was cast into a square plate measuring 4 × 10 × 10 mm. The porcelain specimen was also formed into a square plate measuring 4 × 10 × 10 mm. The 10 × 10 mm surfaces of the alloy plate and porcelain plate were polished with #1000 sand paper. The polished surface was used as the adherend. The adherend was covered with a piece of adhesive tape having a hole 5 mm in diameter. This hole establishes the area of bonding. On the other hand, a stainless steel round rod measuring 7 mm in diameter and 30 mm long was provided. The end of the rod was polished by sandblasting with alumina barasive having an average particle diameter of 33 μm. Formulation 5 and formulation 6 were mixed in equal quantities. The resulting viscous paste was thickly applied to the end of the stainless steel rod. Immediately after application, the end of the stainless steel rod was pressed perpendicularly against the adherend of the Ni—Cr alloy specimen and the porcelain specimen. After adhesion, the specimens were dipped in water at 37°C for 3 days. The tensile bonding strength was measured on an Instron tensile tester (at a crosshead speed of 2 mm/min).

In the case of Ni—Cr alloy, the cohesive failure of the adhesive occurred in all of ten specimens tested, and the average bonding strength was 27 MPa (275 kg/cm^2).

In the case of porcelain, both interfacial failure (at porcelain side) and cohesive failure occurred, and the average bonding strength was 14 MPa (146 kg/cm^2).

Comparative Example 3

Formulation 7 was prepared according to the following composition, in which compound (E) has the following formula



(E)

	Parts by weight
Formulation 7.	
Methyl methacrylate	98
Compound (E)	2
Benzoyl peroxide	2
MEHQ	trace amount

Formulation 7 was combined with formulation 6 in Example 3 to give a powder-liquid type adehsive. The bonding test was carried out in the same manner as in Example 3. After dipping in water at 37°C for 3 days, bonding strength was measured. The bonding strength for the Ni—Cr alloy specimen was 9.6 MPa (98 kg/cm^2) and that for the porcelain specimen was 5 MPa (52 kg/cm^2).

Example 4

A powder-liquid type adhesive of the following composition was prepared from the compound (B) synthesized in Production Example 2.

	Parts by weight
Formulation 8.	
2,2-Bis[methacryloyloxypolyethoxyphenyl]propane	60
1,6-Hexanediol dimethacrylate	30
Compound (B)	10
Benzoyl peroxide	2
MEHQ	trace amount

Formulation 9.

Silane-treated quartz powder	100
Sodium benzenesulfinate	0.6
N,N-diethanol-p-toluidine	0.6

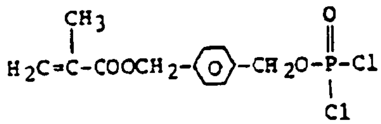
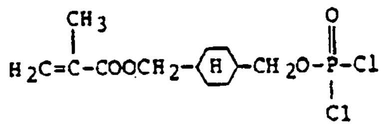
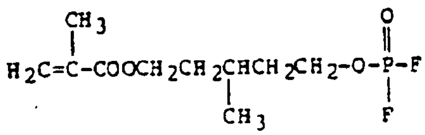
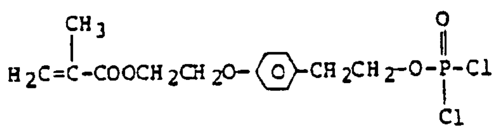
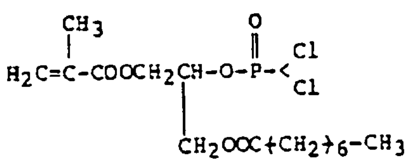
The resulting adhesive was evaluated with respect to adhesion of the dental Co—Cr alloy to a bovine tooth.

The Co—Cr alloy (Co: 62%, Cr: 32%, Mo: 3.5%, others: 2.5%) was cast into a round rod, 5 mm in diameter and 15 mm long. The end of the rod was polished by sand-blasting. On the other hand, the enamel surface of the bovine tooth was polished with #1000 sand paper to make a flat surface on which to stand the above-mentioned round rod. The flat surface underwent acid etching with 40% aqueous solution of phosphoric acid. Formulation 8 and formulation 9 were mixed in a ratio of 1:3.5. The resulting pasty adhesive was applied to the end of the round rod of Co—Cr alloy. The end of the rod was pressed against the etched enamel surface. The superfluous paste which had been forced out was removed carefully. After being kept pressed for 1 hour, the specimens were dipped in water at 37°C for 1 month. The bonding strength was measured on an Instron tensile tester. The average bonding strength of five specimens was 12.5 MPa (128 kg/cm^2). Failure occurred at the interface between the adhesive and the enamel surface.

Examples 5 to 9

Adhesives were prepared in the same way as in Examples 1 and 3 from the compounds listed in Table 1. Their bonding strength for the dentin of human teeth, the Ni—Cr alloy, and the dental porcelain was measured as in Examples 1 and 3. The results are shown in Table 1.

Table 1

Example No.	Compound	Bonding strength in kg/cm² (MPa): Human teeth	Ni-Cr alloy	Porcelain
5		65 (6.4)	230 (22.5)	108 (10.6)
6		66 (6.5)	196 (19.2)	102 (10.0)
7		60 (5.9)	173 (17.0)	84 (8.2)
8		71 (7.0)	301 (29.5)	115 (11.3)
9		55 (5.4)	207 (20.3)	92 (9.0)

Example 10

As the adherends, round rods measuring 7 mm in diameter and 25 mm long were prepared from iron, aluminum, copper, α-alumina, glass, polymethyl methacryalte, and polycarbonate. The end of each rod was polished with #1000 silicon carbide sand paper.

Formulation 5 and formulation 6 in Example 3 were mixed in equal quantities. The resulting pasty adhesive was applied to the polished end of the rod, and two rods of the same kind were butted together. After 1 hour, the bonded specimens were dipped in water at room temperature for 1 week. The tensile bonding strength was measured. The results are as follows:

Iron	:	332 kg/cm² (32.6 MPa)
Aluminum	:	296 kg/cm² (29.0 MPa)
Copper	:	218 kg/cm² (21.4 MPa)
α-Alumina	:	235 kg/cm² (23.0 MPa)
Glass	:	96 kg/cm² (9.4 MPa)
Polymethyl methacrylate	:	191 kg/cm² (18.7 MPa)
Polycarbonate	:	152 kg/cm² (14.9 MPa)

Comparative Example 4

The same adhesive as in Example 3 was prepared except that the compound (B) in formulation 5 was replaced by a compound of the formula

$$CH_2{=}CH(C_6H_6)CH_2OP\begin{matrix}\diagup Br\\ \diagdown Br\end{matrix}$$

which is described in Japanese Patent Laid-open No. 151607/1982. The resulting adhesive was evaluated in the same way as in Example 10. The tensile bonding strength for iron, aluminum, copper, α-alumina, and glass was lower than 4.9 MPa (50 kg/cm^2), and that for polymethyl methacrylate and polycarbonate was lower than 14.7 MPa (150 kg/cm^2).

Example 11

A cylindrical cavity measuring 4 mm in diameter and 4 mm deep was formed on the lingual surface of a human molar by using a diamond bur. The cavity was dried by using an air syringe. A mixture of equal quantities of formulation 1 and formulation 2 in Example 1 was applied to the entire cavity wall. Air was blown to the coated surface by using an air syringe to vaporize ethanol. A commercial dental composite resin "Clearfil-F" was filled in the cavity in the usual way. The tooth specimen was dipped in water at 37°C for 1 day. Then, the tooth specimen was dipped in water at 4°C and water at 60°C alternately 100 times for 1 minute each. The water was colored with a dye. The tooth specimen was cut with a cutter to see if the dye had infiltrated into the interface between the tooth and the filling material. The infiltration of the dye was not found at all.

Example 12

A conical cavity measuring 6 mm in diameter and 4 mm deep was formed on the occlusal surface of a human molar. An inlay that fits in the cavity was cast from type III gold alloy. A 1:3.5 mixture (by weight) of formulation 8 and formulation 9 in Example 4 was applied to the conical surface of the inlay. The inlay was forced into the cavity to effect bonding. After 30 minutes, the tooth specimen was dipped in water at 37°C for 1 day. Then, the tooth specimen was subjected to thermal cycling test by dipping in water at 4°C and water at 60°C alternately. After the test, the inlay stayed in the cavity so firmly that it could not be pried off by a knife tip.

Example 13

A 1-mm thick plate that fits to the lingual surface of a human anterior tooth was prepared by casting from an Ni—Cr alloy (Ni: 76%, Cr: 12% Mo: 3%, others: 9%). The surface of the casting that comes into contact with the tooth was polished by sandblasting with 33-micron alumina abrasive. The lingual surface of the anterior tooth underwent acid etching for 1 minute with 40% aqueous solution of phosphoric acid.

A 1:3.5 mixture (by weight) of formulation 8 and formulation 9 in Example 4 was applied to the surface of the casting. The casting was bonded to the lingual surface of the anterior tooth. After 10 minutes, the bonded specimens were dipped in water at 37°C for 1 day. The tensile bonding strength was 16.1 MPa (164 kg/cm^2). Interfacial failure occurred at the tooth surface.

Example 14

A pit and fissure sealant for filling the fissure of a molar was prepared according to the following composition.

	Parts by weight
Formulation 10.	
2,2-Bis(methacryloyloxypolyethoxyphenyl)propane	60
Neopentylglycol dimethacrylate	30
Compound (A)	10
Benzoil peroxide	2

Formulation 11.

Bis-GMA	40
HEMA	40
Neopentylglycol dimethacrylate	20
Sodium benzenesulfinate	2
N,N-diethanol-p-toluidine	2

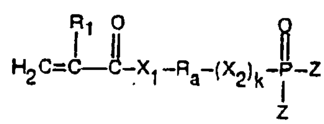
The fissure of a human molar was cleaned with an explorer, followed by washing and drying. The sealant (a 1:1 mixture of formulation 10 and formulation 11) was filled in the fissure without etching. Ten minutes after curing, the tooth specimen was dipped in water at 37°C for 1 day. Then, the tooth specimen was dipped in water at 4°C and water at 60°C alternately 100 times for 1 minute each. The water was colored with a dye. The tooth specimen was cut with a cutter to see if the dye had infiltrated into the interface between the tooth and filling material. The infiltration of the dye was hardly found.

Example 15

A cylindrical cavity measuring 4 mm in diameter and 4 mm deep was formed on the buccal surface of a human molar by using a diamond bur. The cavity wall underwent acid etching for 1 minute with 40% aqueous solution of phoshporic acid, followed by washing and drying. The paste obtained by mixing formulation 8 and formulation 9 in Example 4 in the ratio of 1:3.5 by weight was filled in the cavity. Ten minutes after curing, the tooth specimen was dipped in water at 37°C for 1 day. Then, the infiltration of dye into the bonding interface was examined in the same manner as in Example 4. The infiltration of the dye was hardly found.

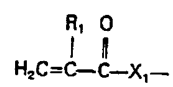
Claims

1. An adhesive comprising (a) 1 part by weight of a polymerizable monomer represented by the formula:

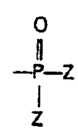


(1)

In which k is 0 or 1, R_1 is a hydrogen atom or methyl radical; R_a is a C_{6-40} organic residue not containing an

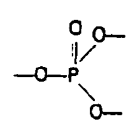


group and not containing a



group; each of X_1 and X_2, which are the same or different, is an oxa or thia group or a group NR′, where R′ is a hydrogen atom or a C_{1-6} hydrocarbon group, and Z is a halogen atom (F, Cl, Br or I); and (b) 0 to 199 parts by weight of monomer that is copolymerizable with said monomer (a).

2. An adhesive as claimed in Claim 1 or 2, in which R_a is (i) a C_{6-30} hydrocarbon group, optionally having halogen, hydroxyl or carboxyl substitution, or (ii) a C_{6-30} organic residue in which two to seven C_{1-29} hydrocarbon groups, at least one of which has 3 or more carbon atoms, and any or all of which optionally has or have halogen, hydroxyl or carboxyl substitution, are connected to one another through a —O—, —S—, —COO—, —CSO—, —COS—, —CS—, —NR′CO—, —NHCOO—, —CO—, —SO_2, —N<, or

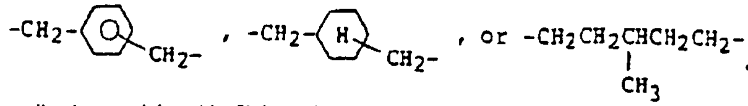


linkage, where R' denotes H or a C_{1-6} hydrocarbon group.

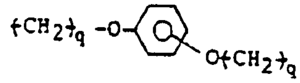
3. An adhesive as claimed in Claim 2, in which k is 1, and X_1 and X_2 are —O—.

4. An adhesive as claimed in Claim 3, in which R_a is $—(CH_2)_n—$ where n is an integer from 6 to 20.

5. An adhesive as claimed in Claim 3, in which R_a is



6. An adhesive as claimed in Claim 3, in which R_a is



where q is 2, 3 or 4.

7. An adhesive as claimed in Claim 3, in which R_a is

$$\begin{array}{l} —CH_2CH— \\ \quad\quad\;\; | \\ \quad\quad CH_2O(CO)_p—R_b \end{array}$$

where p is 0 or 1 and R_b is a C_{3-16} hydrocarbon group.

8. An adhesive as claimed in Claim 1, in which 0.01 to 20 parts by weight of a curing agent is incorporated per 100 parts by weight of the polymerizable monomers (a) + (b).

9. An adhesive as claimed in Claim 8, in which the curing agent is redox-type polymerization initiator or a photosensitizer.

10. An adhesive as claimed in any preceding claim, in which a volatile organic solvent having a boiling point lower than 150°C at 760 Torr is incorporated, the amount of it being less than 300 times (by weight) the weight of the polymerizable monomers (a) + (b).

11. An adhesive as claimed in any preceding claim, in which 20 to 500 parts of a filler is incorporated per 100 parts by weight of the polymerizable monomers (a) + (b).

12. An adhesive as claimed in preceding claim, in which the vinyl monomer (b) is of the (meth)acrylate ester or styrene type or a vinyl acetate.

13. A dental adhesive as claimed in Claim 8 or 9 or as claimed in Claim 10 as dependent on Claim 8 or 9, for use in applying to the wall of tooth cavity before filling a dental composite resin into the tooth cavity.

14. An adhesive as claimed in Claim 11 as dependent on Claim 8 or 9, for use in filling into a tooth cavity.

15. An adhesive as claimed in Claim 11 as dependent on Claim 8 or 9 for use in bonding between a tooth and a dental restorative material or between dental restorative materials.

16. A dental adhesive as claimed in Claim 8 or 9, for use in coating a tooth surface for prevention of dental caries.

17. An adhesive as claimed in Claim 9, in which the curing agent is an initiator of the redox type, made up into two or three packs, one of which contains the oxidizing component and the other(s) the or each reducing component of the initiator, the other ingredient being distributed between the packs.

18. An adhesive as claimed in Claim 8 made up into two packs, in which the curing agent is in one pack and the vinyl monomer (b) in the other.

Patentansprüche

1. Klebstoff aus (a) 1 Gew.-Teil eines polymerisierbaren Monomeren der Formel

$$H_2C=\overset{R_1}{\overset{|}{C}}—\overset{O}{\overset{\|}{C}}—X_1—R_a—(X_2)_k—\overset{O}{\overset{\|}{\underset{Z}{\underset{|}{P}}}}—Z \quad (I)$$

worin k 0 oder 1, R_1 ein Wasserstoffatom oder ein Methylrest, R_a ein organischer C_{4-40}-Rest ist, der keine

$$H_2C=\overset{R_1}{\overset{|}{C}}—\overset{O}{\overset{\|}{C}}—X_1 \text{ -Gruppe}$$

und keine

$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Z}{|}}{P}}-Z \text{ -Gruppe}$$

enthält, jeder der Substituenten X_1 und X_2, die gleich oder verschieden sind, eine Oxa- oder Thiagruppe oder eine Gruppe NR' ist, wobei R' ein Wasserstoffatom oder eine C_{1-6}-Kohlenwasserstoffgruppe ist, und Z ein Halogenatom (F, Cl, Br oder J) ist, und (b) 0 bis 199 Gew.-Teilen eines Monomeren, das mit dem Monomeren (a) copolymerisierbar ist.

2. Klebstoff nach Anspruch 1, worin R_3 (i) eine C_{8-30}-Kohlenwasserstoffgruppe, gegebenenfalls mit einer Halogen-, Hydroxyl- oder Carboxylsubstitution, oder (iii) ein organischer C_{8-30}-Rest ist, in welchem 2 bis 7 C_{1-29}-Kohlenwasserstoffgruppen, von denen wenigstens eine 3 oder mehr Kohlenstoffatome besitzt und irgendeine oder alle davon gegebenenfalls eine Halogen, Hydroxyl- oder Carboxyl-Substitution aufweist bzw. aufweisen, miteinander über eine —O—, —S—, —COO—, —CSO—, —COS—, —CS—, —NR'CO—, —NHCOO—, —CO—, —SO_2—, —N<, oder

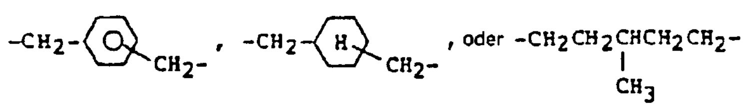
$$-O-\overset{\overset{\displaystyle O}{\|}}{P}\begin{matrix} O- \\ \\ O- \end{matrix}$$

Verknüpfung verbunden sind, worin R' für H oder eine C_{1-6}-Kohlenwasserstoffgruppe steht.

3. Klebstoff nach Anspruch 2, worin k 1 ist und X_1 und X_2 —O— sind.

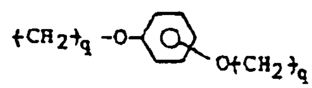
4. Klebstoff nach Anspruch 3, worin R_a —$(CH_2)_n$—, worin n eine ganze Zahl von 6 bis 20 ist, bedeutet.

5. Klebstoff nach Anspruch 3, worin R_a



ist.

6. Klebstoff nach Anspruch 3, worin R_a



wobei q 2, 3 oder 4 ist, bedeutet.

7. Klebstoff nach Anspruch 3, worin R_a

$$\begin{matrix} -CH_2CH- \\ | \\ CH_2O(CO)_p-R_b \end{matrix}$$

wobei p 0 oder 1 ist und R_b eine C_{2-18}-Kohlenwasserstoffgruppe ist, bedeutet.

8. Klebstoff nach Anspruch 1, worin 0,01 bis 20 Gew.-Teile eines Härtungsmittels pro 100 Gew.-Teile der polymerisierbaren Monomeren (a) + (b) eingemengt sind.

9. Klebstoff nach Anspruch 8, worin das Härtungsmittel ein Redoxtyp-Polymerisationsinitiator oder ein Fotosensibilisator ist.

10. Klebstoff nach einem der vorhergehenden Ansprüche, worin ein flüchtiges organisches Lösungsmittel mit einem Siedepunkt von weniger als 160°C bei 760 Torr eingemengt ist, dessen Menge weniger als das 300-fache (bezogen auf das Gewicht) des Gewichts der polymerisierbaren Monomeren (a) + (b) beträgt.

11. Klebstoff nach einem der vorhergehenden Ansprüche, worin 20 bis 500 Teile eines Füllstoffs pro 100 Gew.-Teile der polymerisierbaren Monomeren (a) + (b) eingemengt sind.

12. Klebstoff nach einem der vorhergehenden Ansprüche, worin das Vinylmonomere (b) ein (Meth)acrylatester oder eine Styroltyp oder ein Vinylacetat ist.

13. Dentalklebstoff nach Anspruch 8 oder 9 oder nach Ansoruch 10 in Abhängigkeit von Anspruch 8 oder 9 für eine Verwendung zur Aufbringung auf die Wand einer Zahnkavität vor dem Einfüllen eines Dentalverbundharzes in die Zahnkavität.

14. Klebstoff nach Anspruch 11 in Abhängigkeit von Anspruch 8 oder 9 für eine Verwendung zum Einfüllen in eine Zahnkavität.

15. Klebstoff nach Anspruch 11 in Abhängigkeit von Anspruch 8 oder 9 für eine Verwendung in einer Bindung zwischen einem Zahn und einem Zahnreparaturmaterial oder zwischen Zahnreparaturmaterialien.

16. Dentalklebstoff nach Anspruch 8 oder 9 für eine Verwendung in einem Überzug einer Zahnoberfläche zur Verhinderung einer Zahnkaries.

17. Klebstoff nach Anspruch 9, in welchem das Härtungsmittel ein Initiator des Redoxtyps ist, das in zwei oder drei Packungen verpackt ist, von denen eine die oxidierende Komponente und die andere(n) die oder jede reduzierende Komponente des Initiators enthält (enthalten), wobei der andere Bestandteil zwischen den Packungen verteilt ist.

18. Klebstoff nach Anspruch 8, verpackt in zwei Packungen, wobei sich das Härtungsmittel in einer Packung und das Vinylmonomere (b) in der anderen Packung befindet.

Revendications

1. Un adhésif comprenant (a) partie en poids d'un monomère polymérisable représenté par la formule:

$$H_2C{=}C(R_1)-C(=O)-X_1-R_a-(X_2)_k-P(=O)(Z)-Z \qquad (I)$$

dans laquelle k est 0 ou 1, R_1 est un atome d'hydrogène ou un groupe méthyle; R_a est un reste organique en C_{5-40} ne contenant pas de groupe

$$H_2C{=}C(R_1)-C(=O)-X_1-$$

et ne contenant pas de groupe

$$-P(=O)(Z)-Z;$$

chacun de X_1 et X_2, qui sont semblables ou différents, est un groupe oxa ou thia ou un groupe NR' où R' est un atome d'hydrogène ou un groupe hydrocarboné en C_{1-6} et Z est un atome d'halogène (F, Cl, Br ou I); et (b) 0 à 199 parties en poids d'un monomère copolymérisable avec ledit monomère (a).

2. Un adhésif selon la revendication 1, où R_a est (i) un groupe hydrocarboné en C_{6-30} ayant facultativement une substitution halogène, hydroxyle ou carboxyle, ou (ii) un reste organique en C_{6-30}, dans lequel 2 à 7 groupes hydrocarbonés en C_{1-29}, dont au moins un a 3 ou plus de 3 atomes de carbone et dont un nombre quelconque a facultativement une substitution halogène, hydroxyle ou carboxyle sont raccordés entre eux par une liaison —O—, —S—, —COO—, —CSO—, —COS—, —CS—, —NR'CO—, —NHCOO—, —CO—, —SO_2—, —N< ou

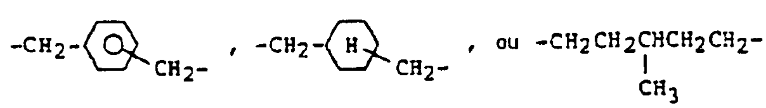
$$-O-P(=O)(O-)(O-),$$

où R' représente H ou un groupe hydrocarboné en C_{1-6}.

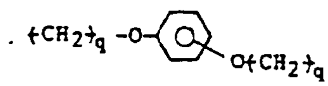
3. Un adhésif selon la revendication 2, où k est 1 et X_1 et X_2 sont —O—.

4. Un adhésif selon la revendication 3, ou R_a est —$(CH_2)_n$— où n est un entier de 6 à 20.

5. Un adhésif selon la revendication 3, où R_a est



6. Un adhésif selon la revendication 3, où R_3 est



où q est 2, 3 ou 4.

7. Un adhésif selon la revendication 3, où R_a est

$$-CH_2CH- \atop \qquad\quad | \atop \qquad\qquad\quad CH_2O(CO)_p-R_b$$

en C_{3-16}.

8. Un adhésif selon la revendication 1, dans lequel 0,01 à 20 parties en poids d'un agent de durcissement sont incorporées pour 100 parties en poids des monomères polymérisables (a) + (b).

9. Un adhésif selon la revendication 8, dans lequel l'agent de durcissement est un amorceur de polymérisation de type redox ou un photosensibilisateur.

10. Un adhésif selon l'une quelconque des revendications précédentes, dans lequel un solvant organique volatil ayant un point d'ébullition inférieur à 150°C à 101 kPa (760 torrs) est incorporé, sa quantité étant inférieure à 300 fois (en poids) le poids des monomères polymérisables (a) + (b).

11. Un adhésif selon l'une quelconque des revendications précédentes, dans lequel 200 à 500 parties d'une charge sont incorporées pour 100 parties en poids des monomères polymérisables (a) + (b).

12. Un adhésif selon l'une quelconque des revendications précédentes, dans lequel le monomère vinylique (b) est du type ester (méth)acrylique ou styrène ou un acétate de vinyle.

13. Un adhésif selon la revendication 8 ou 9 ou selon la revendication 10 rattachée à la revendication 8 ou 9, pour l'emploi dans l'application à la paroi d'une cavité dentaire avant l'obturation de la cavité dentaire avec une résine composite dentaire.

14. Un adhésif selon la revendication 11 rattachée à la revendication 8 ou 9, pour l'emploi dans l'obturation d'une cavité dentaire.

15. Un adhésif selon la revendication 11 rattachée à la revendication 8 ou 9, pour l'emploi dans l'union d'une dent et d'un matériau de restauration dentaire ou l'union de matériaux de restauration dentaire.

16. Un adhésif dentaire selon la revendication 8 ou 9, pour l'emploi dans le revêtement d'une surface dentaire pour la prévention des caries dentaires.

17. Un adhésif selon la revendication 9, dans lequel l'agent de durcissement est un amorceur de type redox constitué de deux ou trois composants dont l'un contient le composant oxydant, et le ou les autres le ou chaque composant réducteur de l'amorceur, l'autre ingrédient étant réparti entre les deux composants.

18. Un adhésif selon la revendication 8 constitué de deux composants, dans lequel l'agent de durcissement est dans un composant et le monomère vinylique (b) dans l'autre.